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Approved For Release 2009/08/06 : CIA-RDP80T00246A009700440001-6

SUMMARY

The anomalies of electrical and magnetic properties in invars at low temperatures and the fact that these anomalies are observed in iron-nickel alloys with the nickel content ranging from 30 to 40 percent are explained on the grounds of an assumption that the exchange integral of electrons of neighboring ions of iron in a face-centred lattice is negative which entails a "latent" antiferromagnetism in the invars. This assumption is founded on experimental data obtained by authors and proving that in an iron alloy with a face-centered lattice, stable at low temperature thanks to the presence of chrominium and nickel alloying elements, an antiferromagnetic transformation occurs. The paper presents results of investigation of the influence of pressure upon the magnetic saturation σ_s and the residual resistivity ρ. of iron, nickel and iron-nickel alloys at low temperatures. It is hown that the values $K_\sigma = \frac{1}{\sigma_s}\frac{\Delta\sigma_s}{\Delta p}$ and $K_\rho = \frac{1}{\rho_0}\frac{\Delta\rho}{\Delta p}$ in invar alloys at low temperatures and other iron-nickel alloys; the ratios K_ρ / K_σ are approximately equal to the ratios $\frac{1}{\rho}\frac{\Delta\rho}{\Delta H} / \frac{1}{\sigma}\frac{\Delta\sigma}{\Delta H}$ which is in agreement with the conclusions of the suggested theory.

Fig I a

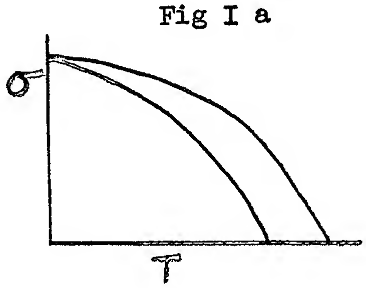
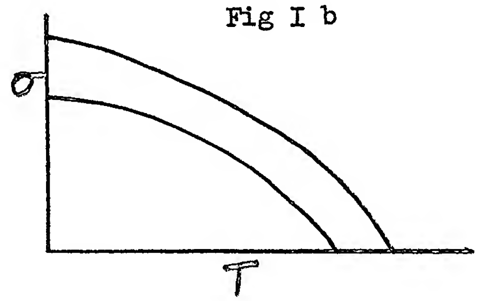


Fig I b



ANTIFERROMAGNETISM OF IRON IN FACE-CENTERED CRYSTALLINE LATTICE AND THE CAUSES OF ANOMALIES IN INVAR PHYSICAL PROPERTIES

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The physical properties of 36 percent Ni invar alloys have a number of anomalies (I): the low heat expansion coefficient, a substantial value of electrical resistivity, comperatively big values of volume magnetostriction, magnetic susceptibility in the magnetic saturation region and the coefficient $K_\sigma = \frac{1}{\sigma}\frac{\Delta \sigma_s}{\Delta p}$ describing the pressure influence upon the specific magnetic saturation σ_s. It follows from the thermodynamic equality: $\frac{1}{V}\left(\frac{\partial V}{\partial H}\right)_p = \left(\frac{\partial I_s}{\partial p}\right)_H$ that at big values of K_σ, big values of volume magnetostriction should be observed in invars and as a sequence the heat expansion coefficient anomalies. The comparatively big values of K_σ in invars have been explained heretofore (2-4) by the assumption that the exchange interaction energy between the electrons of neighboring ions in these alloys changes radically under the expansion or compression of the crystalline lattice. It was believed that the point corresponding to the mean exchange integral for ions in invars is on the steep part of the positive section of the Bete-Slaiter curve, and it has been considered that the changes in the spontaneous magnetization of these alloys caused by pressure come as a sequence of the Curie point displacement which in its turn is related to the change in the exchange energy which the distance between the lattice ions shrinks or increases. Fig.I-a shows how the spontaneous magnetization should change under the influence of pressure if the latter caused only the Curie point shift.

This explanation of the K_σ anomaly and of the related peculiarities of physical properties in invar alloys can hardly be treated as a satisfactory one. It doesn't supply a direct an answer as to why these anomalies are observed precisely in the iron-nickel alloys with nickel concentration ranging from 30 to 45 percent or in iron-platinum alloys at definite concentrations, and is not observed in these alloys with some other contents of nickel or platinum. There are also doubts as to the validity of comparing the dependence curve of Curie temperature upon the nickel concentration in iron-nickel alloys with the Bete-Slaiter curve. Finally, from the point of view of the above said concepts it is impossible to explain the high electrical resistivity and a number of anomalies in magnetic properties that have been recently found (5-7) in invars at low temperatures. In their paper (7) the authors of the present work have shown that the limit value of magnetic saturation $\sigma_0 = (\sigma_s)_{T=0}$ and the residual resistivity ρ, change with hydrostatic compression, and that the coefficients $(K_\sigma)_{T=0}$ and $(K_\rho)_{T=0}$ do not turn into zero. Thus, the actual shape of the curve for the invar alloys at $P > 0$ is not as is shown in Fig I-a outline, but follows the pattern of Fig. Ib. Apparently, the changes of σ_s due to the pressure in the low temperature region (the left part of the curve in Fig. Ib)cannot be explained by the Curie point displacement due to pressure.

In the paper (7) we have indicated the possible causes of pressure influence upon σ_0 and ρ_0, in particular that the changes of σ_0 and ρ_0 can be a result of the influence of pressure upon the values of the d-d exchange integrals provided certain exchange integrals are negative and there is a non-compensated antiferromagnetism in the alloy. The present work attempts to explain the anomalies of electrical and magnetic properties in invars at low temperatures and that these anomalies are manifest precisely at a nickel content

ranging from 30-40 percent, preceeding from the assumption that the exchange integral of the electrons of the neighbouring iron ions in a face-centered lattice is negative.

I. Experimental Grounds for Supposing that Iron is Antiferromagnetic in a Face-centered Lattice

It has been shown in paper (8) that for the γ -phase (face-centered cubic lattice) of iron in the temperature interval from 910-1400°C when the phase is stable, the Curie-Weiss law is valid but with other values of the C and θ parameters than for the α -phase (body-centered cubic lattice). In keeping with the paper (8) the θ parameter for the γ -iron phase is a negative value (θ_{γ} --1340°K), which gives us grounds to suppose the absence of the ferromagnetic trans-formation in this phase up to the absolute zero. In order to determine whether the γ -phase of iron is paramagnetic or antiferromagnetic at low temperatures we should prevent the $\gamma \rightarrow \alpha$ transition by introducing alloying elements and by appropriate heat treatment. The paper (9) has a brief reference to, the fact that according to the neutronographic analysis data the $Fe-Mn$ alloys with a face-centered cubic lattice containing over 12 percent of manganese are antiferromagnetic. However, thusfar no works have been published where these data would have been described.

We have investigated the temperature dependence of the magnetic susceptibility of an alloy with a face-centered lattice, containing 73 percent of iron, 18 percent of chromium and 9 percent of nickel. No precipitate of the ferromagnetic α -phase at low temperature has been observed in the alloys of this content that have been aged at room temperature following their preparation (10). The specific susceptibility χ was measured by means of the procedure described by me in paper (7), The results are presented in Fig 2. The antiferromagnetic

transformation takes place at $40^{o}K$. The value of the paramagnetic Curie point proves to be $-28\pm3^{o}K$.

The obtained results give grounds to suppose that the exchange interactions in a face-centered iron lattice would at low temperatures result in antiferromagnetism similarly to the neighbouring elements manganese (11-12) and chromium (13), and the exchange integral of the d electrons of the neighbouring ions of iron.

2. Anomalies in invar alloys magnetic and electrical properties at low temperatures

The magnetic saturation I_s of iron-nickel alloys at hydrogen temperatures has been studied in the work of Kondorsky and Fedotov (14). In paper (15) and in our paper (7) we have studied the residual electrical resistivity of these alloys. Fig. 3 presents the curves describing the dependence $I_0 = (I_s)_{T=0}$ and $\mathcal{S}_0$ of iron-nickel alloys upon nickel content. In the invar alloy region there takes place a decrease of I_0 and a radical growth of $\mathcal{S}_0$ at the increase of the iron content.

In order to determine how far the $K_\sigma = \frac{1}{\sigma}\frac{\Delta\sigma_s}{\Delta P}$ and $K_\rho = \frac{1}{\rho}\frac{\Delta\rho}{\Delta P}$ differ for invar alloys from the same values in the alloys of other content we have studied the influence of pressure upon σ_0 and $\mathcal{S}_0$ of iron, nickel, and iron-nickel alloys of different concentration.

A pressure of about 150 atm. was created by gaseous helium which was fed into a beryllium-bronze bomb from a gas tank through a capillar valve. The bomb with the specimen was in a field of a water-cooled sollemoid. The measuring coils, the basic and the compensating one were placed outside the bomb and were in the circuit of the photoelectrical fluxmeter, with the sensitivity of 5 Maxwell/dag. The error in measuring the value $\frac{\Delta I_s}{\Delta P}$ was $\pm 0.15 \cdot 10^{-4}$ Gauss/atm. The value was determined by the procedure described in papers (16-17). In this case

the pressure was created by freezing a 3 percent aqueous solution of alcohol.

It turned out that within the accuracy limits of our measurements the values R_σ of the studied metals and alloys are not dependent on temperature in the range from 4.2 to 20.4°K, while in the same interval K_R values slowly diminish with temperature.

Fig. 4 presents the curves describing the dependence of the K_σ and K_ρ limit values obtained by extrapolation to absolute zero, from the nickel content in the alloys. In the region of invar alloys (30-40%) there takes place a radical increase of R_σ and a peak K_ρ. Thus, the K_σ anomaly in the invars takes place both at high and low temperatures.

3. Ferromagnetism-Antiferromagnetism Transformation in Iron-Nickel Alloys With Face-centered Lattice as the Cause of Anomalies in Magnetic and Electrical Properties of Invars

The quantum-mechanical calculation of the magnetic saturation of disordered alloys involves profound mathematical difficulties and thusfar has not been carried out. A calculation of this type for the ordered AB and AB_3 alloy has been performed by Kondorsky and Pakhomov (18) but the results cannot be applied to disordered alloys like invars. Therefore, proceeding fromthe quasi-classical model we shall try to make a rough estimate of the least nickel concentration in iron-nickel alloys at which these alloys can be ferromagnetic, provided that the exchange integral of the d electrons of the neighbouring ions of iron is negative. Suppose $\mathcal{J}$, $\mathcal{J}_{12}$ and $\mathcal{J}_2$ are exchange integrals d electrons of neighbouring ions of iron, iron and nickel and nickel, respectively: C_1 and C_2 - are the concentrations of iron and nickel in the alloy ($C_1 - C_2 = 1$). The concentrations of ions of iron and nickel with the right and left spins shall be denoted as C_1^+, C_2^+, C_1^-, and C_2^- respectively.

As has been indicated for the first time by Vonsovsky (19) it is impossible to consider the spontaneous magnetization of parts of the lattice occupied by ions

of nickel separately from the parts of the lattice occupied by the ions of iron but rather only the full numbers of r and ℓ of right and left spins respectively. Therefore we should take $C_1^+ = \frac{r}{2n} C_1$, $C_2^+ = \frac{r}{2n} C_2$, $C_1^- = \left(1 - \frac{r}{2n}\right) C_1$, $C_2^- = \left(1 - \frac{r}{2n}\right) C_2$, where $2n = r + \ell$.

Then considering the mean exchange energies of iron and nickel ions with right and left spins surrounded by Z neighbours, (Z=12) and taking into account only the interaction between the neighbouring ions it is not difficult to obtain for the exchange energy Wa alloy from N ions.

$$W_a = \frac{NZ}{2}\left(\frac{r}{n} - 1\right)^2 \left(C_1^2 J_1 + 2 C_1 C_2 J_{12} + C_2^2 J_2\right) \qquad (I)$$

which coincides with the formula obtained for the first time in the work (19).

It follows from (I) that at low temperatures the antiferromagnetism is possible provided there are negative exchange integrals. The pure nickel is ferromagnetic, within an increase of the iron content up to 60 percent the magnetic moment of iron-nickel alloys increases too Hence $J_2 > 0$, $J_{12} > 0$. In view of the experimental data that have been mentioned earlier we may take $J_1 < 0$. Then the state with $r = 2n$, i. e., a ferromagnetic state, will correspond to the smallest values of the exchange energy Wa when the trinominal in the second brackets (I) is positive. When this trinominal is negative the least value of Wa is obtained at $r = n$ which corresponds to antiferromagnetism. Hence, if we have the $C_2 > C_R$ concentration, the ferromagnetism is more advantageous from the energy point of view at low temperatures, if $C_2 < C_{R}$ then under the same condition the antiferromagnetism is more advantageous. Taking the trinominal in the formula (I) as being equivalent to zero we find that

$$C_R = \frac{J_{12} - J_1 - \sqrt{J_{12}^2 - J_1 J_2}}{2 J_{12} - J_1 - J_2} \qquad (2)$$

in a special case when $-J_1 \approx J_{12} \approx J_2$, $C_R \approx 0.3$ which, apparently, is a quite satisfactory result.

The random distribution of ions with anti-parallel spins is more likely

at high temperatures then at low ones when there should take place the groupings of spins (the closest magnetic order). Therefore between the fully ferromagnetic and the antiferromagnetic there should be alloys with some of the ions having the anti-parallel spins. This type of "latent" antoferromagnetism should take place when the mean energy of the ion of iron with the left spin $W^- = z\left(\frac{2}{n} - 1\right)(J_1 C_1 + J_{12} C_2)$ is negative, i.e. at a nickel concentration of $C_2 < C_0 = -\frac{J_1}{J_{12} - J_1}$. Hence at $-J_1 \approx J_{12}$, $C_0 \approx 0.5$. While $C_{12} > C_0$ the ferromagnetic moment of iron-nickel alloys grows linearly with the increase in the iron content, at $C_2 = C_0$ appears a deviation from linearity and at C_2 close to C_R there sets in a radical drop of I., thanks to an increase in the number of the anti-parallel spins. As it is seen from Fig. 3, the change in the I. with the growth of iron content in the iron-nickel alloys with the face-centered lattice occurs precisely in this way. Let us note that the deviation from the linearity in the curve I. occurs in the interval of nickel content ranging from 50 to 40 percent, while with further decrease in nickel content, beginning with 40 percent a radical drop of I. is observed.

We believe that the latent antiferromagnetism should be regarded as the main cause of the anomalies in invar physical properties. In fact, the presence of the anti-parallel spins in these alloys explains the comparatively big values of the volume magnetistriction and the susceptibility of the paraprocess in strong magnetic fields. Further, as it is seen from formula (I) the transitional concentration C_R grows with the increase in the absolute value J_1, which most likely grows at hydrostatic compression[x)]. An increase in C_R entails a shift of the steep part of the curve I. towards the nickel and which should be accompanied by radical decrease in I. and σ, precisely of the invars which are in the transition region. As it is seen from Fig. 4 the experimental data corroborate this conclusion.

x) Let us note that too explain the C_R "displacement" there is no necessity of

assuming that any of exchange integrals correspond to the point on the steep part of the Bete-Slaiter curve and are more sensitive to the changes of the inter-atomic distances that others. For instance from (2) at $-J_1 = J_{12} = J_2$ and $\frac{dJ_1}{d\rho} = \frac{dJ_{12}}{d\rho} = \frac{dJ_2}{d\rho} = \frac{dJ}{d\rho}$ it follows that $\frac{dC_{12}}{d\rho} = -\frac{1}{2\sqrt{2}J_1}\frac{dJ}{d\rho}$. Then if $\frac{dJ}{d\rho} > 0$ we find $\frac{dC_{12}}{d\rho} > 0$.

In a similar way it is possible to explain the anomaly of magnetic properties observed in iron-platinum alloys at platinum content of 30-40 percent. The exchange integral J_2 of d-electrons of neighboring ions of platinum should be taken as equivalent to zero, since up to helium temperatures platinum remains paramagnetic. Since iron-platinum alloys are ferromagnetic, $J_{12} > 0$. Taking $J_1 < 0$ just as in the iron nickel alloys we shall obtain from (2) for concentration C_R of iron-platinum alloys $C_R = -\frac{J_1}{2J_{12} - J_1}$ that at $-J_1 > J_{12}$ gives $C_R = 0.33$. If platinum concentration $C_2 > C_R$ the alloys are ferromagnetic. Substituting in (2) the sign minus before the radical for plus at the same values of the exchange integrals we shall find that ferromagnetism in iron-platinum alloys disappear at iron concentration close to zero.

An indirect confirmation of "latent" antoferromagnetism in invars is their great electrical resistivity, which we believe is due to the conductivity electron scattering on the magnetic moment heterogeneities. With an increase in the iron content from 50 percent the electrical resistivity begins to grow and particularly vigorously in the region of the magnetic moment drop. As a value describing the magnetic moment of anti-parallel spins we may regard $I_o = I_o - I_c$ where I_c - is the spontaneous magnetization value corresponding to the ordinate obtained by extrapolating the linear part of the I_o curve on the iron and (Fig.5). I_c - are the spontaneous magnetization values of alloys with x concentrations in real or hypothetical case when all the spins are parallel. If we determine the $\Delta \rho$ electrical resistivity incriments and the ΔI_o spontaneous

magnetisation, which correspond to the increase in the iron concentration on ΔC, compose the ratios $\frac{1}{\rho_0}\frac{\Delta\rho}{\Delta C} / \frac{1}{I_0}\frac{\Delta I_0'}{\Delta C}$ and compare them with the ratios $\frac{1}{\rho}\frac{\Delta\rho_1}{\Delta H} / \frac{1}{\sigma_0}\frac{\Delta\sigma_0}{\Delta H}$ and K_ρ / K_σ for the alloys of the same concentrations, it turns out that all these ratios are approximately the same. Table I presents the values of these ratios for the alloys with the nickel content of 34.7 percent and 38 percent.

The value $\frac{1}{\rho_1}\frac{\Delta\rho_1}{\Delta H}$ in strong fields is negative in ferromagnetics and ordinarily this has been associated with the fact that when the true magnetization grows in the strong fields the scattering of electrons on spin waves decreases. The "latent" antiferromagnetism considered by us in invar alloys is reduced to the existence of spin waves at absolute zero. An approximate confidence of the mentioned ratios may be regarded therefore as a confirmation of the assumption on the "latent" antiferromagnetism.

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Table I

	Content of nickel in alloy	
	[illegible]	[illegible]
$\frac{1}{\rho_0}\frac{\Delta\rho_0}{\Delta c} \Big/ \frac{1}{I_0}\frac{\Delta I_0'}{\Delta c}$	-3	-4
$\frac{1}{\rho_0}\frac{\Delta\rho_0}{\Delta H} \Big/ \frac{1}{\sigma_0}\frac{\Delta\sigma_0}{\Delta H}$	0	-1.1
A_ρ / A_σ	-1.7	-7.4
$\frac{\Delta\rho_0}{\Delta c} \Big/ \frac{\Delta\sigma'}{\Delta c}$ x) $\mu\Omega\, G^{-1} g\, cm^{-3}$	-0.9	-0.8
$\frac{\Delta\rho_0}{\Delta H} \Big/ \frac{\Delta\sigma_0}{\Delta H}$ $\mu\Omega\, G^{-1} g\, cm^{-3}$	0	-0.6
$\frac{\Delta\rho}{\Delta p} \Big/ \frac{\Delta\sigma_0}{\Delta p}$ $\mu\Omega\, G^{-1} g\, cm^{-3}$	-2.3	-2.4

x) $\sigma_0' = \frac{I_0'}{\delta}$, δ - density of alloy.

Captions

Fig.I. Diagram of pressure influence upon spontaneous magnetisation.

a) The spontaneous magnetisation alters only due to Curie point shift.

b) The spontaneous magnetisation alters due to Curie point shift and due to the change in the average atomic magnetic moments.

Fig.2. The temperature dependence of the magnetic susceptibility and it inverse value in austenite steel with 18% Cr and 9% Ni. Fracture points indicating the antiferromagnetic transformation.

Fig.3. Magnetic saturation at absolute zero point and residual resistivity of iron-nickel alloys versus nickel content in alloys o o c / Δ Δ Δ unordered alloys (Data of Authors and of paper (8)

Λ Λ — ordered alloys (Data of paper (8)).

Fig.4. Values of $A_\sigma = \frac{1}{\sigma_0}\frac{\Delta\sigma}{\Delta p}$ and $A_\rho = \frac{1}{\rho_0}\frac{\Delta\rho}{\Delta p}$ versus nickel content in iron-nickel alloys. The curves exhibit the anomalies of A_σ and A_ρ in invare region.

Fig.5. Diagram illustrates the determination of I_0' and I_c.

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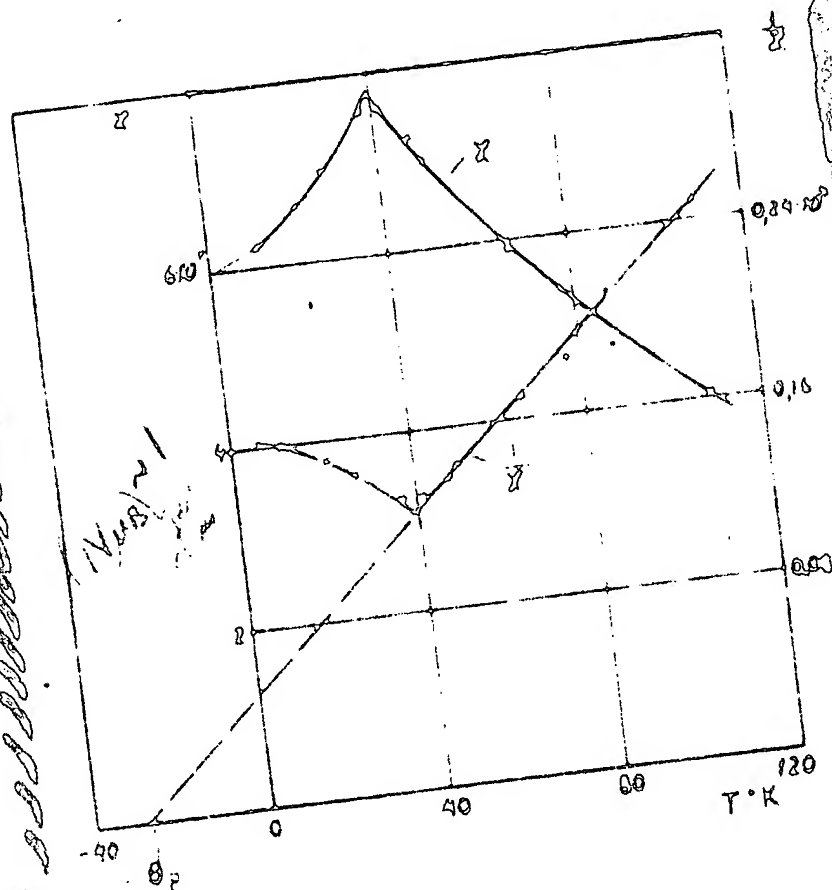

From Wul Data
X ray $a_0 = 3.59$ Å
$N = \frac{4 \cdot 10^{24}}{(3.59)^3} = 8.6 \times 10^{22}$

$C = \frac{N g^2 S(S+1) \mu_B^2}{3k}$

$\chi(T+\theta)\,3k$
$N g^2 S(S+1)$

6×10^{-4}

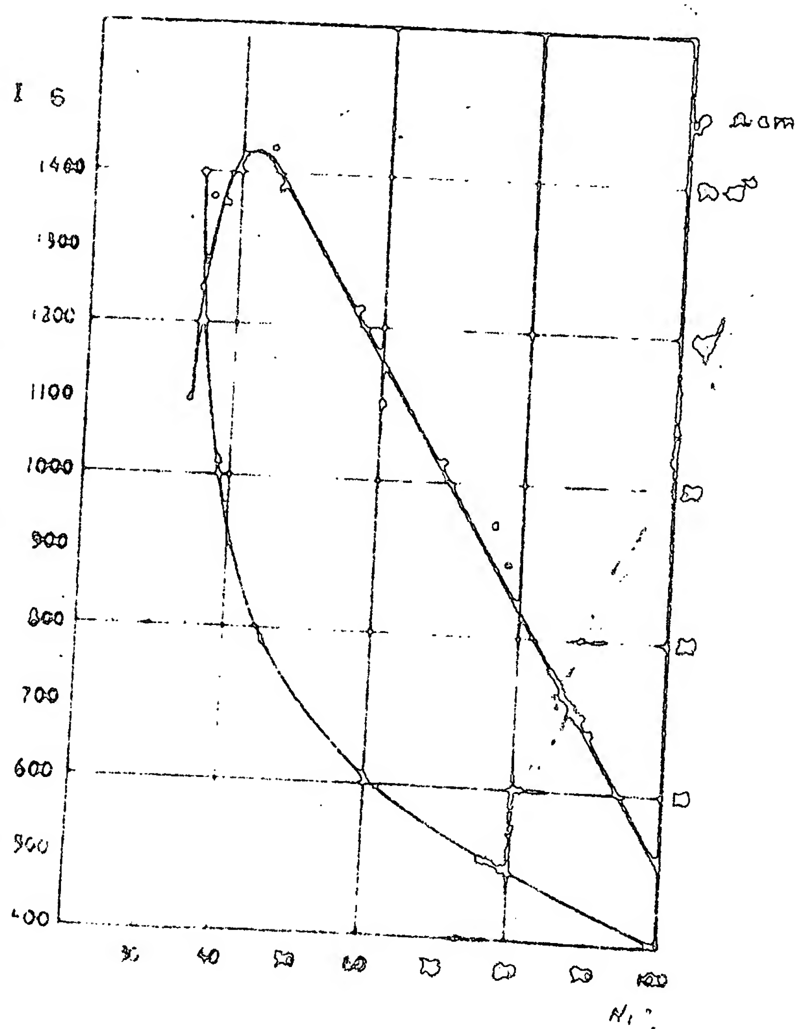
1400
1100
1000
900
800
700
600
40
60
100

Fig. 1

T=0°K